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R&T Code 413p009--05

Technical Report No. 7

Synthesis and Properties of Homonuclear, Dimetallic Nickel(II),
Copper(II) and Zinc(II) Complexes of p-Xylenediyl
and 2-Butynediyl-Bridged Dicyclens

by

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Manuscript submitted to *Inorganic Chemistry*

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May, 1993

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE				Form Approved GMB No 0704 0188	
1a REPORT SECURITY CLASSIFICATION Unclassified			1b RESTRICTIVE MARKINGS		
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION/AVAILABILITY OF REPORT		
2b DECLASSIFICATION/DOWNGRADING SCHEDULE			Distribution Unlimited		
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 7			5 MONITORING ORGANIZATION REPORT NUMBER(S)		
6a NAME OF PERFORMING ORGANIZATION Research Foundation of SUNY		6b OFFICE SYMBOL (If applicable) SUNY	7a NAME OF MONITORING ORGANIZATION Office of Naval Research		
6c ADDRESS (City, State, and ZIP Code) State University of NY Stony Brook, NY 11794			7b ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington, VA 22217		
8a NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b OFFICE SYMBOL (If applicable) ONR	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-88-K-0315		
8c ADDRESS (City, State, and ZIP Code) Chemistry Division 800 N. Quincy Street Arlington, VA 22217-5000			10 SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO	PROJECT NO	TASK NO
					413P
					413P009-05
11 TITLE (Include Security Classification) Synthesis and Properties of Homonuclear, Dimetallic Ni(II), Cu(II) and Zn(II) Complexes					
12 PERSONAL AUTHOR(S) Christopher G. Crane and Cynthia J. Burrows					
13a TYPE OF REPORT Manuscript		13b TIME COVERED FROM _____ TO _____		14 DATE OF REPORT (Year, Month, Day) 93/05/31	
				15 PAGE COUNT 12	
16 SUPPLEMENTARY NOTATION Submitted to: <u>Inorganic Chemistry</u>					
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
19 ABSTRACT (Continue on reverse if necessary and identify by block number) Two new dinucleating ligands have been prepared by linking two [12]-aneN ₄ (cyclen) macrocycles with either a p-xylenediyl or a 1,4-butanediyl bridge. The nickel(II), copper(II) and zinc(II) dinuclear complexes have been fully characterized. Their design was intended to be a mimic of the dinuclear hydrolytic enzyme urease which contains two nickel ions in the active site. Catalytic hydrolysis studies are in progress.					
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a NAME OF RESPONSIBLE INDIVIDUAL Dr. Harold E. Guard			22b TELEPHONE (Include Area Code) (202) 696-4311		22c OFFICE SYMBOL ONR

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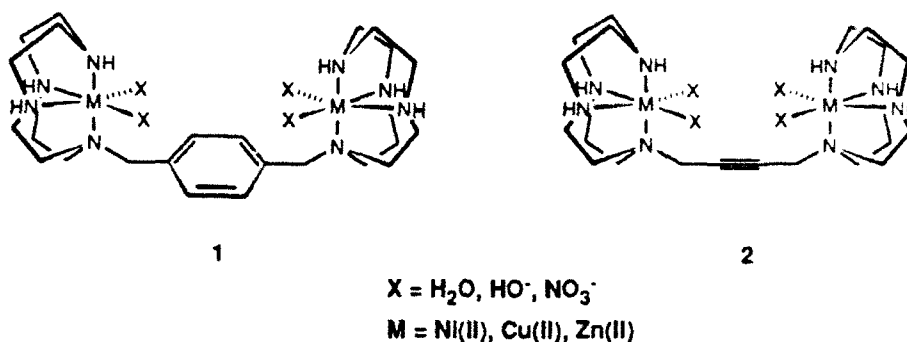
Christopher G. Crane and Cynthia J. Burrows*

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Introduction

Many mononuclear complexes of nickel(II),^{1,2} copper(II)³⁻⁵ and especially zinc(II)⁶⁻¹⁰ have been used to promote the hydrolysis of carboxylate and phosphate esters as models for hydrolytic metalloenzymes. In contrast, the enzyme urease has been shown to contain two nickel(II) ions in the active site,¹¹ but as yet the exact nickel-nickel distance is not known. In efforts to understand the roles of two metal ions in catalytic hydrolysis, dinucleating ligands incorporating the macrocycle cyclen have been designed. The ligands α,α' -*p*-xylenediylbis(1,4,7,10-tetraazacyclododecane), **1**, and 1,4-but-2-ynediylbis(1,4,7,10-tetraazacyclododecane), **2**, were synthesized and the dinickel(II), dicopper(II) and dizinc(II) complexes were subsequently prepared.

These molecules contain two key features. First, the two 1,4,7,10-tetraazacyclododecane (cyclen) groups are linked by a rigid spacer group (either *p*-xylenediyl



or 2-butyndiyl) forcing the formation of dinuclear rather than mononuclear species. The metal-metal distances are estimated to be 3.7 and 3.3 Å, respectively, when the cyclen macrocycles assume a syn conformation.¹² The formation of a sandwich complex around one metal ion is not possible. Secondly, the relatively small macrocycle cyclen can only coordinate to four mutually cis sites of a metal ion in octahedral geometry. This leaves vacant coordination sites with cis geometry free for the binding of water molecules, hydroxide ions, and a substrate ester, amide or urea.

Experimental Section

1. Materials. 1,4,7,10-tetraazacyclododecane (cyclen) tetrahydrogen chloride was purchased from Parish Chemical Company and converted to the free amine by passage down an ion-exchange column (Dowex 1X8-100) in the hydroxide form. 1,4-Bis(4-methylbenzenesulfonyl)-but-2-yne was prepared by the method of Jaworski et al.¹³ $[\text{Ni}(\text{cyclen})(\text{NO}_3)](\text{NO}_3)$ and $[\text{Cu}(\text{cyclen})(\text{NO}_3)](\text{NO}_3)$ were synthesized according to the methods of Smieriak et al.¹⁴ and Styka et al.,¹⁵ respectively. Other commercial reagents were used as obtained without further purification. Acetonitrile was dried by standing over molecular sieves (class 3 Å, 8-12 mesh) for 24 hours.

2. Physical Measurements. Melting points (mp) were measured with a Thomas

Hoover capillary melting point apparatus below 200°C and with a Mel-temp apparatus above 200°C. IR spectra were recorded as KBr pellets on a Perkin-Elmer 1600 series FT-IR. Absorbances are listed in cm^{-1} as weak (w), medium (m), strong (s), shoulder (sh) or broad (br). ^1H and ^{13}C NMR were recorded on a General Electric QE-300 (300MHz for ^1H and 75MHz for ^{13}C). Chemical shifts (δ) are referenced to TMS in organic solvents and DSS in D_2O . Multiplicities are as follows: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet and br=broad. UV/visible spectra were obtained on a Hewlett Packard 8452A diode array spectrophotometer using quartz cells. Fast atom bombardment (FAB) mass spectra were performed on a Kratos 80 in either nitrobenzyl alcohol (NBA) or glycerol (GLY) matrix. Elemental analysis were performed by Atlantic Microlab. Inc., Norcross, GA. Conductivity measurements were performed with a Fisher Scientific conductivity meter (09-327). Potentiometric titrations were performed with the aid of a Metrohm 655 "Dosimat" micrometer driven syringe, the pH being measured with a Corning ion analyzer 250. In a typical experiment 5.0mL of a $2 \times 10^{-3}\text{M}$ solution (in M^{2+}) containing 0.1M NaClO_4 was titrated with 0.1M CO_2 -free solution of NaOH at 40°C.

3. Syntheses. (a) Synthesis of α,α' -p-xylenediylbis(1,4,7,10-tetraazacyclododecane).

1. To cyclen (2.654g, 15.4mmol) and anhydrous K_2CO_3 (2.13g, 15.4mmol) suspended in dry acetonitrile (20mL) at reflux under dinitrogen was added dropwise over 1h α,α' -dibromo-*p*-xylene (163mg, 0.616mmol) dissolved in dry acetonitrile (10mL). The mixture was allowed to reflux overnight, filtered while hot, and the residue washed with hot acetonitrile (2x10mL). The filtrates were combined and the solvent removed under reduced pressure. The excess cyclen was removed by sublimation (0.2mmHg, 90°C) to leave the product. Yield: 255mg, 93%. IR (KBr): $\nu(\text{NH})$ 3255, s. ^1H NMR (CDCl_3): δ 7.29 (s, 4H, ArH), 3.60 (s, 4H, ArCH_2N), 2.88-2.46 (m, 38H, NCH_2 and NH). ^{13}C NMR (CDCl_3): δ 139.1 and 129.1 (ArC).

59.9 (ArCH₂N), 51.2, 46.4, 45.9 and 44.5 (NCH₂). FAB⁺ MS (GLY): m/z 447, (M+H)⁺.

Note: Synthesis of **1** was previously reported with no experimental details.¹⁶

(b) Synthesis of 1,4-but-2-yne-diylbis(1,4,7,10-tetraazacyclododecane), 2. This ligand was prepared by a similar reaction to **1**, replacing the dibromoxylene with 1,4-bis(4-methylbenzenesulfonyl)-but-2-yne. Yield = 88%. ¹H NMR (CDCl₃): δ 3.46 (s, 4H, CCH₂N), 2.78-2.53 (m, 38H, NCH₂ and NH). ¹³C NMR (CDCl₃): δ 79.4 (CCH₂), 50.2 (CCH₂), 47.1, 46.4, 44.9 and 43.5 (NCH₂). FAB⁺ MS (NBA): m/z 395, (M+H)⁺.

(c) Synthesis of [Zn(cyclen)(NO₃)](NO₃). This complex was prepared by the same method as Ni(cyclen)(NO₃)₂ replacing Ni(NO₃)₂ with Zn(NO₃)₂·6H₂O. Yield of white microcrystals 70%, mp dec.>290°C. IR (KBr): ν(NH) 3178, s; ν(NO₃) 1384, s. Electronic spectrum (H₂O): λ (ε) 302 nm (16). ¹H NMR (D₂O): δ 2.98-2.74 (m, NCH₂). Anal. Calcd for C₈H₂₀N₆O₆Zn: C, 26.57; H, 5.57; N, 23.24. Found: C, 26.68; H, 5.56; N, 23.14.

(d) Synthesis of [Ni₂(1**)(NO₃)_{4-x}](NO₃)_x.** To **1** (50mg, 0.112mmol) dissolved in absolute ethanol (5mL) was added Ni(NO₃)₂·6H₂O dissolved in absolute ethanol (10mL). The mixture was refluxed for 20min, allowed to cool to room temperature and the hygroscopic, purple product collected by filtration. Yield: 64.4mg, 71%. IR (KBr): ν(NH) 3221, s; ν(NO₃) 1385, s. Electronic spectrum (H₂O): λ (ε) 356nm (87), 440nm (26), 580nm (33). FAB⁺ MS (NBA): 750 [(M-NO₃)⁺], 688 [(M-2NO₃)⁺], 626 [(M-3NO₃)⁺], 564 [(M-4NO₃)⁺], 502 [(M-4NO₃-Ni)⁺]. Anal. Calcd for C₂₄H₄₆N₁₂Ni₂O₁₂: C, 35.50; H, 5.71; N, 20.70. Found: C, 35.02; H, 5.75; N, 19.59.

(e) Synthesis of [Cu₂(1**)(NO₃)_{4-x}](NO₃)_x.** This complex was prepared by the same method as Ni₂(**1**)(NO₃)₄ replacing Ni(NO₃)₂ with Cu(NO₃)₂·3H₂O. Yield of hygroscopic, blue powder 71%. IR (KBr): ν(NH) 3192, s; ν(NO₃) 1385, s. Electronic spectrum (H₂O): λ (ε) 594nm (689). FAB⁺ MS (NBA): 757 [(M-NO₃)⁺], 695 [(M-2NO₃)⁺], 633 [(M-3NO₃)⁺], 570

[(M-4NO₃)⁺], 507 [(M-4NO₃-Cu)⁺]. Anal. Calcd for C₂₄H₄₆Cu₂N₁₂O₁₂: C, 35.08; H, 5.64; N, 20.45. Found: C, 35.60; H, 5.66; N, 19.81.

(f) **Synthesis of [Zn₂(1)(H₂O)(NO₃)_{4-x}](NO₃)_x.** This complex was prepared by the same method as Ni₂(1)(NO₃)₄ replacing Ni(NO₃)₂ with Zn(NO₃)₂·6H₂O. Yield of white powder 64%. IR (KBr): ν(NH) 3228, s; ν(NO₃) 1383, s. Electronic spectrum (H₂O): λ (ε) 296nm (112). ¹H NMR (D₂O): δ 7.45 (s, 4H, ArH), 4.05 (s, 4H, ArCH₂N), 3.28-2.72 (m, 32H, NCH₂). ¹³C NMR (D₂O): δ 132.2 & 131.6 (Ar), 55.7 (ArCH₂N), 49.4, 44.8, 44.0 & 42.4 (NCH₂). FAB⁺ MS (NBA): 762 [(M-NO₃)⁺], 699 [(M-2NO₃)⁺], 634 [(M-3NO₃)⁺], 570 [(M-4NO₃)⁺], 507 [(M-4NO₃-Ni)⁺]. Anal. Calcd for C₂₄H₄₈N₁₂O₁₃Zn₂: C, 34.18; H, 5.74; N, 19.93. Found: C, 34.44; H, 5.48; N, 19.57.

(g) **Synthesis of [Ni₂(2)(NO₃)_{4-x}](NO₃)_x.** This complex was prepared by the same method as Ni₂(1)(NO₃)₄ replacing 1 by 2. Yield of hygroscopic, purple powder 54%. IR (KBr): ν(NH) 3261, s; ν(NO₃) 1385, s. Electronic spectrum (H₂O): λ (ε) 304 (126), 352 (83), 562nm (20). FAB⁺ MS (NBA): 696 [(M-NO₃)⁺], 633 [(M-2NO₃)⁺], 569 [(M-3NO₃)⁺]. Anal. Calcd for C₂₀H₄₂N₁₂Ni₂O₁₂: C, 31.60; H, 5.57; N, 22.12. Found: C, 31.29; H, 5.85; N, 20.89.

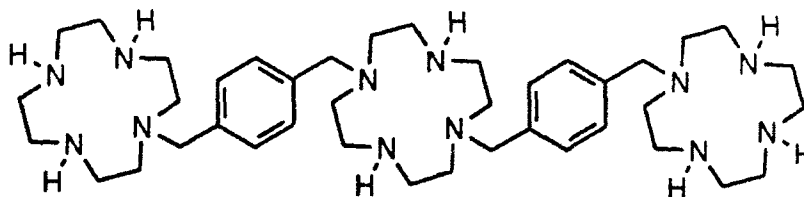
(h) **Synthesis of [Cu₂(2)(NO₃)_{4-x}](NO₃)_x.** This complex was prepared by the same method as Ni₂(1)(NO₃)₄ replacing Ni(NO₃)₂ with Cu(NO₃)₂·3H₂O and 1 by 2. Yield of hygroscopic, blue powder 71%. IR (KBr): ν(NH) 3144, s; ν(NO₃) 1385, s. Electronic spectrum (H₂O): λ (ε) 600nm (574). FAB⁺ MS (NBA): 706 [(M-NO₃)⁺], 644 [(M-2NO₃)⁺], 582 [(M-3NO₃)⁺], 517 [(M-4NO₃)⁺], 460 [(M-4NO₃-Cu)⁺]. Anal. Calcd for C₂₄H₄₆Cu₂N₁₂O₁₂: C, 31.20; H, 5.50; N, 21.84. Found: C, 30.22; H, 5.48; N, 20.76.

(i) **Synthesis of [Zn₂(2)(H₂O)(NO₃)_{4-x}](NO₃)_x.** This complex was prepared by the same method as Ni₂(1)(NO₃)₄ replacing Ni(NO₃)₂ with Zn(NO₃)₂·6H₂O and 1 by 2. Yield of

pale yellow powder 64%. IR (KBr): $\nu(\text{NH})$ 3228, s; $\nu(\text{NO}_3)$ 1383, s. Electronic spectrum (H_2O): λ (ϵ) 308nm (192). ^1H NMR (D_2O): δ 3.97 (br s, 4H, $\text{CCCH}_2\text{NCH}_2$), 3.68 (s, 4H, CCCH_2), 3.04-2.74 (m, 24H, NCH_2). ^{13}C NMR (D_2O): δ 79.4 (CC), 50.4 (CCCH_2), 44.6, 43.8, 42.9 and 42.3 (NCH_2). FAB⁺ MS (NBA): 712 [(M- NO_3)⁺], 584 [(M-3 NO_3)⁺], 521 [(M-4 NO_3)⁺], 460 [(M-4 NO_3 -Zn)⁺]. Anal. Calcd for $\text{C}_{20}\text{H}_{44}\text{N}_{12}\text{O}_{13}\text{Zn}_2$: C, 30.35; H, 5.60; N, 21.24. Found; C, 30.55; H, 5.46; N, 21.05.

Results and Discussion

A. Synthesis of the Dinuclear Complexes. The synthesis of ligands **1** and **2** was inspired by the work of Alcock et al.^{17,18} in which excess cyclen as nucleophile was allowed to react with a suitably substituted linking group such as a dibromide. It was found that at least a 25:1 excess of cyclen was needed to prevent significant formation of a product containing 3 cyclen moieties linked by 2 spacer groups such as **3**. Cyclen was recovered pure after sublimation for reuse. The product was then isolated in quite pure form as the residue. The dinuclear complexes **1** and **2** were easily formed by reaction with simple metal nitrates in ethanol.



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B. Characterization of the Complexes.

(a) **Solid state.** According to the infrared data (Table 1) all the dimetallic complexes contain water. Interestingly, the complex of zinc nitrate with cyclen does not. This is in variance

with the previously reported work of Norman⁷, who mistakenly assigned a dimetallic structure to the complex between zinc perchlorate and cyclen. Elemental analysis, however, points to a monometallic complex, $[\text{Zn}(\text{cyclen})(\text{H}_2\text{O})](\text{ClO}_4)_2$. Furthermore, Curtis and Curtis¹⁹ found that the ν_2 out-of-plane deformation of the nitrate group is very indicative of the type of nitrate groups present. Thus, we observe resonances at 806 and 825 cm^{-1} , which strongly suggest that the complex contains both a bidentate (chelating) nitrate and an ionic nitrate. Both dinickel complexes were also found to contain only bidentate and ionic nitrates but, the dicopper and dizinc complexes show resonances for bidentate, monodentate and ionic nitrate. However, as no complex of this type containing a bidentate bridging nitrate has been isolated that possibility cannot be ruled out.

(b) Solution state. Conductivity measurements are consistent with the complexes of **1** and **2** existing as hydrated species $[\text{LM}_2(\text{H}_2\text{O})_m]^{4+}$ in solution. A pH titration of the complex $[\text{Zn}(\text{cyclen})(\text{NO}_3)](\text{NO}_3)$ was identical to that obtained by Norman⁷ for the perchlorate salt, confirming that the solution species is a monohydrate. pH titrations of the bimetallic complexes were identical to those of the corresponding monometallic cyclen complexes. For example, $[\text{Zn}(\text{cyclen})(\text{NO}_3)](\text{NO}_3)^{20}$ and $[\text{Zn}_2(\textbf{1})(\text{NO}_3)_{4-x}](\text{NO}_3)_x$ show pK_a 's of 7.8 ± 0.1 and $[\text{Zn}_2(\textbf{2})(\text{NO}_3)_{4-x}](\text{NO}_3)_x$ shows a pK_a of 7.7 ± 0.1 . This would suggest that there is no cooperative effect of the two metal ions in deprotonation of H_2O .

Conclusions

The synthetic method provides ready access to dinucleating ligands with metal-metal distances appropriate for the study of cooperative effects in metal-catalyzed hydrolysis. A disadvantage of this design is that the orientations of the two metal cyclen groups with respect to each other, i.e. *syn* vs. *anti*, are not fixed. If the groups adopt primarily an *anti*

conformation, no cooperativity in deprotonation of water or in metal-hydroxide attack at a coordinated substrate can be expected. Addition of a second bridge linking the cyclen groups would further restrict the conformational mobility, and such work is currently in progress.

Acknowledgements. Support of this research through grants from the National Institutes of Health (GM-34841) and the Office of Naval Research AASERT Program (N0001492J1534) is gratefully acknowledged.

References.

1. Blakeley, R. L.; Treston, A.; Andrews, R. K.; Zerner, B. *J. Am. Chem. Soc.* **1982**, *104*, 612-614.
2. De Rosch, M. A.; Trogler, W. C. *Inorg. Chem.* **1990**, *29*, 2409-2416.
3. Morrow, J. R.; Trogler, W. C. *Inorg. Chem.* **1988**, *27*, 3387-3394.
4. Morrow, J. R.; Trogler, W. C. *Inorg. Chem.* **1989**, *28*, 2330-2333.
5. Chin, J.; Jubian, V. *J. Chem. Soc., Chem. Commun.* **1989**, 839-841.
6. Chin, J.; Zou, X. *J. Am. Chem. Soc.* **1984**, *106*, 3687-3688.
7. Norman, P. R. *Inorg. Chim. Acta* **1987**, *130*, 1-4.
8. Kimura, E.; Koike, T.; Uenishi, K.; Hediger, M.; Kuramoto, M.; Joko, S.; Arai, Y.; Kodama, M.; Iitaka, Y. *Inorg. Chem.* **1987**, *26*, 2975-2983.
9. Kimura, E.; Koike, T.; Nada, H.; Iitaka, Y. *Inorg. Chem.* **1988**, *27*, 1036-1040.
10. Kimura, E.; Koike, T.; Torimuni, K. *Inorg. Chem.* **1988**, *27*, 3687-3688.
11. Dixon, N. E.; Blakeley, R. L.; Zerner, B. *Can. J. Biochem.* **1980**, *58*, 469-473.
12. The dicopper complex of a related ligand incorporating two 12-N,O,S₂ macrocycles shows a metal-metal separation of 3.38 Å when HO⁻ is present as bridging ligand.

- See: (a) Burk, P. L.; Osborn, J. A.; Youinou, M. T.; Agnus, Y.; Louis, R.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1273-1274. (b) Youinou, M. T.; Osborn, J. A.; Collin, J. P.; Lagrange, P. *Inorg. Chem.* **1986**, *25*, 453-461.
13. Jaworski, T.; Prejzner, J.; Terpinski, J. *Roczniki Chemii* **1974**, *48*, 1093-1097.
 14. Smieriak, R. C.; Passariello, J. V.; Blinn, E. L. *Inorg. Chem.* **1977**, *16*, 2646-2648.
 15. Styka, M. C.; Smieriak, R. C.; Blinn, E. L.; DeSimone, R. E.; Passariello, J. V. *Inorg. Chem.* **1978**, *17*, 82-86.
 16. Yaouanc, J.-J.; Le Bris, N.; Le Gall, G.; Clement, J.-C.; Handel, H.; des Abbayes, H. *J. Chem. Soc., Chem. Commun.* **1991**, 206-207.
 17. Alcock, N. A.; McLaren, F.; Moore, P.; Pike, G. A.; Roe, S. M. *J. Chem. Soc., Chem. Commun.* **1989**, 629-632.
 18. For a related synthesis based on cyclen, see: Chung, Y.; Akkaya, E. U.; Venkatachalam, T. K.; Czarnik, A. W. *Tetrahedron Lett.* **1990**, *38*, 5413-5416.
 19. Curtis, N. F.; Curtis, Y. M. *Inorg. Chem.* **1965**, *4*, 804-808.
 20. The pK_a for ligated water deprotonation in this complex was previously reported by Koike and Kimura as 7.9 ± 0.05 in 10% (v/v) aqueous CH_3CN . Koike, T.; Kimura, E. *J. Am. Chem. Soc.* **1991**, *113*, 8935-8941.

Table 1. Water and nitrate ν_2 resonances.

Compound	$\nu_{\text{H}_2\text{O}}$	ν_2^{b}	ν_2^{m}	ν_2^{i}
[Ni(Cyclen)(NO ₃)](NO ₃)	-----	799	-----	825
[Cu(Cyclen)(NO ₃)](NO ₃)	-----	803	-----	825
[Zn(Cyclen)(NO ₃)](NO ₃)	-----	806	-----	825
[Ni ₂ (1)(NO ₃) _{4-x}](NO ₃) _x ·yH ₂ O	3041	805	-----	825
[Cu ₂ (1)(NO ₃) _{4-x}](NO ₃) _x ·yH ₂ O	3436	798	813	825
[Zn ₂ (1)(NO ₃) _{4-x}](NO ₃) _x ·yH ₂ O	3448	797	812	825
[Ni ₂ (2)(NO ₃) _{4-x}](NO ₃) _x ·yH ₂ O	3378	802	-----	825
[Cu ₂ (2)(NO ₃) _{4-x}](NO ₃) _x ·yH ₂ O	3442	796	813	825
[Zn ₂ (2)(NO ₃) _{4-x}](NO ₃) _x ·yH ₂ O	3483	798	813	825

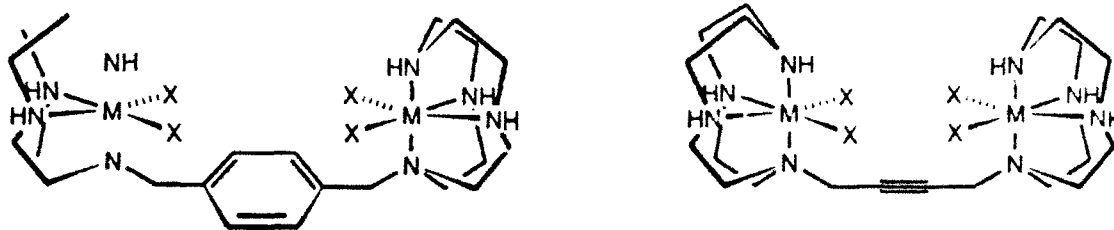
b = bidentate, m = monodentate and i = ionic¹⁸.

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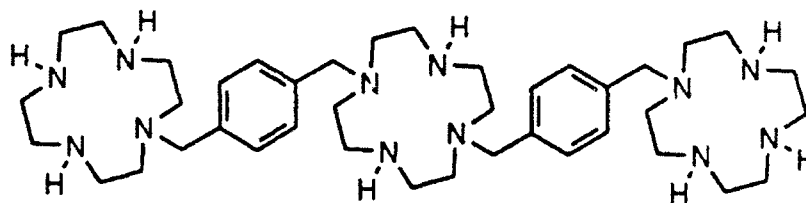
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Abstract: The ligands α,α' -*p*-xylenediylbis(1,4,7,10-tetraazacyclododecane), **1**, and 1,4-but-2-yne-diylbis(1,4,7,10-tetraazacyclododecane), **2**, were synthesized and the dinickel(II), dicopper(II) and dizinc(II) nitrate complexes were prepared and characterized. Both dinickel complexes were also found to contain only bidentate and ionic nitrates but, the dicopper and dizinc complexes show resonances for bidentate, monodentate and ionic nitrate in the solid state. Conductivity measurements are consistent with the complexes of **1** and **2** existing as hydrated species $[\text{LM}_2(\text{H}_2\text{O})_m]^{4+}$ in solution.



$X = \text{H}_2\text{O}, \text{HO}^-, \text{NO}_3^-$
 $M = \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}$



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